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## CIRCUMSTELLAR CHEMISTRY

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## INTRODUCTION

The definitive detection of circumstellar (CS) material around a cool evolved star was made by Deutsch (1956) for  $\alpha$  Her, although the possibility had been discussed as long as 50 years ago. Weymann was one of the first to make physical models of extended envelopes, and in an early review, (Weymann, 1963) wrote "... the pages expended in reviewing the subject (of mass loss)... probably exceed the number of pages of material being reviewed." The situation has since changed dramatically as the result of new observing techniques, particularly in the infrared (IR) and millimeter wave bands. Some of the important early milestones were the observation of IR emission from CS dust, the detection of the 10-micron silicate feature (Woolf and Ney, 1969), the detection of microwave molecular emission from IRC + 10216 (Solomon et al., 1971), and the detection of IR molecular absorption lines (Geballe et al., 1972). These and many other new developments have been followed up by numerous detailed investigations, which have been reviewed previously by Zuckerman (1980).

The observational information available on a few of the closest CS envelopes is now ap-

proaching the stage at which some detailed conclusions on their physical and chemical properties can be obtained. A prime example is the carbon star, IRC + 10216, for which we have extensive data on the spatial and spectral properties of the dust and observations of over 20 molecules (not counting isotopically substituted species). The CS gas around the M supergiant,  $\alpha$  Ori, has also been well studied; in this case, optical observations of atoms and atomic ions play an important role. Better data on more objects will become available as sensitive high-resolution observational techniques are developed.

The data on numerous atomic and molecular species make it possible to investigate the chemical nature of CS shells. Because this is a new area of research, this review must necessarily be fairly qualitative. One long-range goal of the study of CS chemistry is to obtain a sufficiently quantitative description of the constituents so that deductions can be made about the history of the wind material (e.g., the formation of dust) and the tangled problems of stellar evolution and mass loss. The relatively well-ordered gas in the outer parts of the CS envelopes also offers opportunities to understand a number of basic physical and chemical

processes which have applications to the study of interstellar clouds.

After a brief introduction on the physical properties of CS envelopes (see the section *General Physical Considerations*), the bulk of this chapter is divided between a summary of the observations (see the section *Observations*) and a discussion of theoretical considerations concerning the chemistry (see the section *Chemistry*). We conclude with a short summary (see the section *Conclusions*). The literature cited is mainly to articles published before 1984, although references to the major journals for much of 1984 have been included.

## GENERAL PHYSICAL CONSIDERATIONS

This section primarily concerns the massive expanding CS envelopes around the cooler M giants and supergiants, S stars, and the cooler carbon stars. Observational evidence on the physical properties of the envelopes comes from several main lines of investigation: strong continuum emission in the infrared, accompanied by spectral signatures of dust; optical absorption lines of low ionization potential atoms and ions; near-infrared absorption lines of molecules; and microwave molecular emission lines. Details can be found in the review by Zuckerman (1980); observations relevant to chemistry are summarized in the section *Observations*.

Certain basic dynamical and structural facts emerge from the observational data:

1. The terminal wind speeds are small with respect to stellar escape velocities and are typically of the order of  $10 \text{ km s}^{-1}$ .
2. The CS envelopes are large with respect to stellar sizes, ranging up to  $1 \times 10^{18} \text{ cm}$  with corresponding ages up to  $2 \times 10^4 \text{ yr}$ .
3. The mass-loss rates are large, in the range  $10^{-7}$  to  $10^{-4} M_{\odot} \text{ yr}^{-1}$ .

Of course, other detailed dynamical properties are of interest, such as the time dependence of the mass loss (e.g., mass loss may be epi-

sodic) and the detailed spatial variation of the wind density and velocity (e.g., angular as well as radial variations, clumpiness, and shocks). Little is known at present about these issues, but the basic framework given above should be a sufficient starting point for a discussion of the chemistry.

For purposes of simplicity, the winds are often assumed to be spherically symmetric, as well as steady. There are many envelopes which conform to this assumption, at least to first order, and many that do not; only passing reference is made to the latter cases. For the spherically symmetric case, the spatial profile of the mean density of hydrogen nuclei is:

$$n(r) = \frac{C}{r^2} (V/v(r)) , \quad (6-1)$$

$$C = 3 \times 10^{37} \frac{\dot{M}_{-5}}{V_6} \text{ cm}^{-1} , \quad (6-2)$$

where  $V$  is the terminal value for the velocity profile  $v(r)$ , and  $\dot{M}_{-5}$  and  $V_6$  measure the mass-loss rate and velocity in units of  $10^{-5} M_{\odot} \text{ yr}^{-1}$  and  $10 \text{ km s}^{-1}$ , respectively. In a typical case, the outer envelope extends from  $\sim 10^{15}$  to  $10^{17}$  or  $10^{18} \text{ cm}$ ; the corresponding density range is  $\sim 10^6$  to  $10^3$  or  $10^2 \text{ cm}^{-3}$ , roughly the range encountered in interstellar clouds. The temperature profile can also be important for chemical considerations, but little observational information is available on the gas kinetic temperature. Theoretical considerations (heating in gas/dust collisions and cooling by line radiation (Goldreich and Scoville, 1976; Kwan and Hill, 1977; Slavsky and Scalo, 1984)) suggest that the gas kinetic temperature in the outer envelope varies more slowly than the mass density. That is,

$$T(r) \propto r^{-m} , \quad (6-3)$$

with  $m \cong 0.7$ . A typical temperature at  $10^{16} \text{ cm}$  might be of the order of  $100 \text{ K}$ . Closer to the

star the temperature may increase more rapidly than is implied by Equation (6-3), especially if there is a chromosphere.

The temperature and density distributions described above imply that different types of chemistry may dominate in different parts of the envelopes. Beginning just above the photosphere, we may expect to find the conditions for thermal equilibrium to be satisfied. As material moves out into cooler and more rarefied regions, individual species will freeze out when the ratios of appropriate reaction to dynamical time scales exceed unity. Eventually, photochemistry induced by the penetration of galactic UV radiation will dissociate any molecules and ionize the heavy atoms. This qualitative picture becomes more complicated in the presence of active regions associated with a chromosphere or with shocks.

These considerations suggest that the variation in the physical conditions is enormous when we consider the chemical evolution of the wind as it travels from the stellar surface out into the interstellar medium. Furthermore, the formation of dust in the inner envelope is intimately connected with the thermal, dynamical, and chemical evolution of the wind. Not only do space limitations preclude the presentation of such a general discussion of CS chemistry, but, in fact, little research has thus far been done along these lines. Most of the difficult questions about the origin and the physical and chemical properties of the envelopes remain unanswered.

In view of the developing nature of this subject, we have chosen to emphasize the outer parts of the shells ( $r > 10^{15}$  cm) because these appear to be the most accessible to quantitative study at this time. This approach avoids such difficult theoretical questions as the development of the wind and the formation of the dust, but it takes advantage of the main body of currently available observational data. Thus, we emphasize the gas-phase chemistry of the atoms, ions, and molecules outside the region of dust formation. In order to lay the founda-

tions for this study of circumstellar chemistry, we begin by reviewing the observations.

## OBSERVATIONS

This section reviews the observations of CS envelopes which are relevant to a discussion of the chemistry. Many of the observations address more directly other related issues, such as mass loss and dust (see, for example, Zuckerman, 1980; and Goldberg and Lefèvre, this volume), but the concern here is primarily with the gas-phase chemistry. As will become clear, few of the observations directly confront current theoretical ideas, but many more contribute to the development of an overall picture of the physical and chemical properties of the shells. We discuss in turn, hydrogen, the heavy molecules observed in the IR and radiowave bands, and the atoms and ions observed in the optical. Finally, we summarize some other observations which also have a bearing on the chemistry.

### Hydrogen

Although hydrogen is the most abundant element in most stars, it has not yet been observed in atomic (HI) or molecular ( $H_2$ ) form in the extended CS envelopes of cool stars. However, both forms are seen in more evolved objects (see below). Of course, HI is observed in absorption and emission from photospheric and chromospheric regions, but three recent searches for the 21-cm line have failed to reveal HI in the extended envelopes. The searches have been made by Zuckerman et al. (1980), Knapp and Bowers (1983), and Clegg et al. (1983b) using the Arecibo 305-m telescope, the VLA, and the WSRT, respectively. Together, they have surveyed a variety of objects, including M giants and supergiants, C stars, and protoplanetary and planetary nebulae. The Arecibo beamsize ( $3.2'$ ) is comparable to the largest known CS envelope (that of IRC + 10216), whereas the two smaller interferometer beams ( $\sim 15''$ ) could, in principle, spatially resolve a number of the envelopes observed.

Interpretation of the observed upper limits on the 21-cm lines in terms of limits on the HI content of the envelopes is relatively straightforward, apart from the contamination effects of background galactic HI emission and uncertainties in the total masses of the envelopes.

Two results from these surveys deserve special mention. The first is for IRC + 10216, where  $< 1$  percent (or less) of the envelope mass is in the form of HI (Zuckerman et al., 1980; Knapp and Bowers, 1983); the exact limit depends on the adopted total mass of the envelope and the level of significance of the flux limit used. In any event, the absence of HI means that the bulk of the hydrogen must be in molecular form. This result is, perhaps, not too surprising in view of the obvious strong association into molecules evident for other species. However, the limit begins to approach values of interest in connection both with the processes which associate hydrogen molecules in the inner envelope and with photodestruction of  $H_2$  by the ambient galactic UV radiation field. (See the section *Photochemistry*.)

The second limit of particular interest is that for  $\alpha$  Ori. Knapp and Bowers (1983) give a  $5\sigma$  upper limit of  $\dot{M}(\text{HI}) < 5 \times 10^{-6} M_{\odot} \text{ yr}^{-1}$ , which is essentially the same as that given by Clegg et al. (1983b). This value is comparable to many estimates of the total mass-loss rate for the star and is somewhat less than that given by the model of the envelope by Jura and Morris (1981). For an early M supergiant like  $\alpha$  Ori, hydrogen is not expected to be strongly associated into molecules, at least on the basis of the simplest picture of the chemistry. The limits here are then tantalizingly close to confronting the simplest ideas on the HI/ $H_2$  problem. Needless to say, the detection of HI in cool CS envelopes would be a significant contribution to the study of the chemistry.

For completeness, note that the planetary nebulae included in the above surveys also failed to yield detectable HI (see also, Pottasch et al., 1982). Recently, however, Rodriguez and Moran (1983) reported the detection of 21-cm absorption toward NGC 6302 using the VLA.

The absorption is probably associated with the nebula, and they interpret it as arising from the neutral outer part of an expanding ring whose inner part is ionized and produces the thermal continuum. The mass in HI is  $\sim 0.06 M_{\odot}$ .

Although hydrogen must be predominantly in the form of  $H_2$  in the CS envelopes of the coolest stars, it is not observable under normal circumstances. However, IR quadrupole lines of  $H_2$  are seen in absorption in the atmospheres of certain S and carbon Miras, but in other stars, they have generally proved to be much weaker than expected (Tsuji, 1983; Johnson et al., 1983). This possibly indicates that the theoretical atmospheric structures of cool stars are still not well determined or that effects such as chromospheric heating destroy the  $H_2$  in the line-forming regions.

However, the presence of  $H_2$  in CS envelopes can be seen in objects whose central stars have evolved from the cool giant phase.  $H_2$  quadrupole lines in emission have been detected in planetaries and protoplanetaries such as CRL 2688, CRL 618, and NGC 7027 (e.g., Treffers et al., 1976; Beckwith et al., 1978), which still retain many of the CS characteristics of cool stars. Although other interpretations are possible (Black, 1983), the emission appears to be shock-excited and acts as a useful diagnostic of the processes which ionize and dissipate the neutral shell as the central star evolves. The hydrogen molecular ion,  $H_2^+$ , may also have been detected in some planetary nebulae by characteristic continuum absorption in the UV shortward of  $\sim 1500 \text{ \AA}$  (Heap and Stecher, 1981; Feibelman et al., 1981). However, this identification does not appear to be firmly established (see the discussion following Black, 1983).

### Heavy Molecules

The detection of numerous heavy molecules in the CS envelopes of cool stars has been of major significance in understanding processes which occur during the later stages of stellar evolution. The observations yield a variety of

information on the envelope kinematics and mass loss and provide evidence of a rich chemistry. The molecules are detected at radio (mainly millimeter) wavebands in emission and in the IR in absorption. The two techniques are complementary. The IR observations measure vibration-rotation absorption along the line of sight to the continuum-forming regions, whereas the radio measurements sample lower energy (mainly rotational) transitions from the extended envelopes, although the emission is normally not spatially resolved with single antennas. Some symmetric molecules, which possess no permanent dipole moment and thus no rotational spectrum, can be readily detected in the IR.

The C/O ratio dominates the heavy molecule chemistry in stellar photospheres, and this also appears to be true for the CS envelopes.

Therefore, the envelopes of C stars and M and S stars will be discussed separately below.

**IRC + 10216.** Because of its proximity and the richness of its spectrum, IRC + 10216 is by far the most extensively observed CS envelope, and it serves as the prototype for the study of carbon-rich systems. The molecules identified in the envelope are listed in Table 6-1. Most of them have been observed only in the radio, four only in the IR, and three in both. Because most species have been observed in several transitions and/or in isotropically substituted forms, the actual number of lines identified is quite large. There remain several unidentified lines scattered in the literature and a number of upper limits, some of significance. Notably absent are common oxygen-bearing species (e.g., Johansson et al., 1984), except for CO and trace

**Table 6-1**  
**Molecules in IRC + 10216\***

$n(x)/n(\text{CO})$	Species				References <sup>†</sup>
$10^{-1}$	—	—	—	—	
	$\text{C}_2\text{H}_2$				1
$10^{-2}$	HCN	—	—	—	1,2,6
				CN	3
$10^{-3}$	$\text{NH}_3$	—	—	$\text{C}_4\text{H}$	4,5; 6,7
	$\text{C}_2\text{H}_4$	CS	$\text{HC}_5\text{N}$	$\text{C}_2\text{H}$	8; 9,6; 10,6; 3,6
	$\text{CH}_4$	SiS	$\text{HC}_3\text{N}$	$\text{C}_3\text{N}$	1,11; 12,9,16; 13,9,6; 6
$10^{-4}$	—	$\text{SiC}_2$	$\text{HC}_7\text{N}$	—	17;10
	HNC	SiO	$\text{HC}_{11}\text{N}$	$\text{C}_3\text{H}$	6; 9,6; 14; 18,19
$10^{-5}$	—	$\text{SiH}_4$	—	—	15
	$\text{CH}_3\text{CN}$				6

\* For comparison, the reactive radicals, the cyanopolyyne chains, and the S- and Si-bearing molecules are listed separately from the remaining species.

<sup>†</sup> References: 1. Hall and Ridgway (1978), 2. Kwan and Hill (1977), 3. Huggins et al. (1984b), 4. Betz et al. (1979), 5. Kwok et al. (1981), 6. Johansson et al. (1984) (see also Olofsson et al. (1982a), 7. Guelin et al. (1978), 8. Betz (1981), 9. Morris (1975), 10. Winniewisser and Walmsley (1978), 11. Clegg et al. (1982), 12. Henkel et al. (1983), 13. Carlson et al. (1984), 14. Bell et al. (1982), 15. Goldhaber and Betz (1984), 16. Sahai et al. (1984), 17. Thaddeus et al. (1984), 18. Johansson et al. (1984), 19. Thaddeus et al. (1985).

amounts of SiO. This is not too surprising in view of the carbon-rich environment. Also absent are the molecular ions like  $\text{HCO}^+$  and  $\text{N}_2\text{H}^+$  (e.g., Wannier and Linke, 1978), which are readily observable in molecular clouds where their presence is usually interpreted as evidence for a chemistry dominated by ion-molecule reactions.

The interpretation of observed lines, or indeed upper limits, in terms of abundances in the envelope is not straightforward. Because both the radio and IR measurements integrate over regions which are physically, and possibly chemically, inhomogeneous, the results must be treated with some caution.

The IR line measurements are generally interpreted with simple column density arguments, using assumed or measured excitation temperatures to determine partition functions. In some cases, column density estimates may be good to a factor of 3, but are often less accurate. For example, the column densities of  $\text{C}_2\text{H}_2$  (Rinsland et al., 1982) and  $\text{CH}_4$  (Clegg et al., 1982) have recently been revised down by factors of 10 from earlier determinations. The high spectral resolution now attainable with IR instrumentation (Fourier transform spectroscopy and heterodyne techniques) offers opportunities for investigating in detail the kinematics and excitation of molecules in the inner envelope (e.g., Ridgway and Hall, 1980; Betz et al., 1979), but detailed models of this region have not yet been constructed. The possibility of obtaining spatial information from the IR lines has recently been demonstrated (Dyck et al., 1983; Wannier and Sahai, 1983) and will be important for future development.

In contrast to the situation in the IR, fairly complete modeling has been carried out for some species observed in emission in the radio. Kwan and Hill (1977; see also Kwan and Linke, 1982) have shown that the CO rotational levels in IRC + 10216 are primarily excited by collisions; the CO emission is therefore coupled to the gas kinetic temperature. They have developed a thermal model for the gas (including heating by gas/grain collisions and molecular line cooling) and have computed the CO emis-

sivity, convolved with the appropriate beams, for comparison with the observations. They deduce a mass-loss rate for IRC + 10216 of  $4 \times 10^{-5} M_\odot \text{ yr}^{-1}$  (if its distance is 200 pc) and a  $\text{CO}/\text{H}_2$  abundance ratio of  $6 \times 10^{-4}$ . Two aspects of the observations are not completely dealt with in this model: the asymmetry seen in the lines (see, for example, Olofsson et al., 1982a), which may be an effect of radiative transfer or geometry, and the great extent of the CO emission (see Kwan and Linke, 1982). However, neither of these is likely to have much effect on the inferred mass-loss rate or CO abundance.

In the same spirit, Morris (1975) analyzed the emission of high dipole moment molecules in IRC + 10216 and found that their rotational levels are primarily populated by the absorption of IR radiation, followed by rapid decay to different rotational levels of the ground vibrational state. The excitation of these species is therefore coupled to the IR continuum by the absorption-line strengths of the exciting transitions. This kind of model has now been used to analyze a number of species in IRC + 10216: SiS, SiO, CS,  $\text{HC}_3\text{N}$ , CN,  $\text{C}_2\text{H}$ , and HCN (Morris, 1975; Kwan and Hill, 1977; Henkel et al., 1983; Huggins et al., 1984b; Carlson et al., 1985; Sahai et al., 1984; Nguyen-Q-Rieu et al., 1984a). For some of these species, as well as many others not yet analyzed, the IR absorption-line strengths are not (or are poorly) known; however, these are not usually crucial parameters in the analysis. Further complications arise if the molecule has a complex hyperfine structure or if the IR lines are optically thick, but in the best cases, the resulting abundances may be good to a factor of 3. Several other abundance estimates appear in the literature and are based on simplifying assumptions (e.g., beam-averaged column densities or an arbitrarily assumed constant excitation temperature). These should be treated with some caution.

Several tables of abundances for the envelope of IRC + 10216 have been compiled. The early one of McCabe et al. (1979) is not now to be recommended. That of Lafont et al. (1982)

attempts to interpret quoted abundances from a number of different studies in a uniform way. The list of Johansson et al. (1984; see also Olofsson et al., 1982a) is restricted to those species found in the Onsala line survey of IRC + 10216 (which forms an excellent homogeneous data set), but is partially vitiated by the assumption of constant excitation temperatures in the line-forming regions. The abundances quoted for some species differ by a factor of 10 in the last two tables mentioned.

Table 6-1 indicates the approximate abundances of the species observed in IRC + 10216 relative to the CO abundance. The abundances are purposefully given only in decades (with rough ordering within each) so that the reader will not be misled. For the IR data, we use the ratios of column densities, as did Lafont et al. (1982), but with updated values. For the radio-line data, we use the results of model analyses, when available, augmented by other estimates, suitably scaled, where necessary. The references give the most recent analyses and/or primary references from which the earlier results can be found. If more accurate abundance ratios for particular species are required (and are warranted), they can be constructed from the references cited. Implicit in all of the foregoing discussion is the chemical homogeneity of the envelope, which may not be satisfied (see below).

The molecular line observations of IRC + 10216 (and other CS envelopes) are, of course, excellent sources for the determination of isotopic abundances. However, although the observed isotopic ratios are important for understanding nucleosynthesis and envelope mixing processes, they are only indirectly linked to a study of the chemistry of the envelope. Therefore, this subject lies beyond the scope of this chapter, and we refer the reader to the fairly recent reviews by Wannier (1980) and Zuckerman (1980) for further information on this aspect of the observations.

The implications of the observed abundances in IRC + 10216 are discussed in the section *Chemistry*. For convenience, some of the

main points relevant to the chemistry are listed and commented on:

1. The oxygen (i.e., CO) abundance in the gas phase is not very different (a factor  $\sim 3$ ) from solar.
2. In comparison with galactic molecular clouds, HCN is strongly enhanced, by a factor 100 to 1000 if the cloud analyses of Wootten et al. (1978) are used.
3. The absence of molecular ions and O-bearing species (other than CO and SiO) has already been discussed. However, Johansson et al. (1984) have pointed out that the limits on their abundances are not significantly smaller than their observed levels in molecular clouds. However, these species are highly underabundant compared to HCN.
4. The very low value of the isomeric ratio  $\text{HNC/HCN}$  ( $= 4 \times 10^{-3}$ , Johansson et al., 1984) compared to that in molecular clouds has been interpreted (e.g., McCabe et al., 1979; Zuckerman, 1980) as evidence for a simple freeze-out model for these species. Note that because this ratio varies widely in molecular clouds and values as low as  $1.5 \times 10^{-2}$  have been observed (Goldsmith et al., 1981), the argument may not be overly compelling.
5. If the observed Si- and S-bearing species are their major carriers in the gas phase, then, assuming solar abundances, these elements must be highly depleted ( $>95$  percent) into grains. The depletion of other metals is unclear because the lines of their expected major carriers are generally inaccessible. Clegg and Wootten (1980) have searched for AlCl, and find it to be at least 20 times less abundant than would be expected on the basis of

complete association and solar abundances. Cl itself, however, is also not present in the possible alternate form of HCl (Clegg et al., 1982), and it too may be hidden in grains or in more complex molecules.

6. After CO, C<sub>2</sub>H<sub>2</sub>, and HCN, the highly reactive radicals CN, C<sub>2</sub>H, C<sub>3</sub>N, C<sub>4</sub>H, and possibly C<sub>3</sub>H, are as abundant as most of the other molecules observed. Their presence argues strongly against a simple freeze-out process in the inner envelope as the source of their production (Lafont et al., 1982), as discussed in the section *Chemistry*.
7. The significance of the preponderance of linear-chain polyatomics observed in the envelope is not clear. The low abundance of methyl cyanide (CH<sub>3</sub>CN) and the limits on vinyl cyanide (CH<sub>2</sub>CHCN) and ethyl cyanide (CH<sub>3</sub>CH<sub>2</sub>CN) are not particularly stringent when compared to galactic clouds like TMC-1 (cf. Johansson et al., 1984), but they are deficient relative to HCN. The falloff in abundance of the cyanopolyynes with increasing chain length is quite weak: the presence of very large molecules in considerable abundance cannot be ruled out.

We conclude our discussion of IRC + 10216 with a review of the sparse observational data on the spatial extent of the molecules in the envelope. At 100 GHz, the emitting regions of most species are barely resolved with the largest single dishes, so that the information available is very limited. Line profiles provide some information on the extent of the emission, and Olofsson et al. (1982a) have mapped a number of lines to yield characteristic sizes for the emission (e.g., SiO  $\lesssim$  20" and HCN  $\simeq$  40", FWHM). These sizes are probably determined mainly by excitation and optical depth effects and do not readily suggest evidence of spatially

varying abundances. On the other hand, at higher frequencies and increased resolution ( $\sim$  30"), Wootten et al. (1982) have mapped CN in the (2-1) lines and show that it is more extended than HCN, suggesting a possible spatial variation in abundances. Their limit on the absorption column density of CN in the IR is consistent with this, and their data have been shown by Huggins et al. (1984b) to be consistent with a photochemical model in which CN is photoproduced by ambient UV photons from HCN in the outer unshielded envelope. If this proves to be correct, then tables of abundances (e.g., Table 6-2) made assuming constant abundances in the envelope obviously have little meaning.

The CO emission in IRC + 10216 is observable over a much more extended region than other species. Wannier et al. (1979) have shown that the emission is roughly circularly symmetric on a scale of  $\sim$  1'; on a much smaller scale in the optical and near IR, it is not. Knapp et al. (1982) have shown that the emission extends out to a radius of at least 3', which corresponds to a physical radius  $\sim$  0.25 pc for an assumed distance of 290 pc. Since photodestruction must limit the size of molecular shells (e.g., Jura and Morris, 1981; Huggins and Glassgold, 1982a; Lafont et al., 1982), the large extent of the CO emission region yields useful information on this process. Unfortunately, the photodestruction rate and dissociating transitions for CO are poorly known (cf. Glassgold et al., 1985), but Morris and Jura (1983a) have shown that the large map size is consistent with CO line self-shielding.

Finally, note that the new development of interferometry at millimeter wavebands will be useful for more detailed studies of the envelope. A first interferometer map in HCN has been made by Welch et al. (1981) at a resolution of  $\sim$  9". The emission is well resolved and circularly symmetric. Jura (1983a) has argued that the limited extent of the emission implies significant photodestruction of HCN outside a radius of 30" ( $10^{17}$  cm), which is consistent with the photoproduction model for CN mentioned



above. Similar maps of other species, particularly the radicals, will obviously be important in refining our picture of the envelope over the next few years.

**Other Carbon Stars.** In contrast to the fairly extensive observational data on the envelope of IRC + 10216, the available data on other carbon-rich envelopes is very limited. Their lines are generally much weaker because they are farther away and/or have less massive envelopes, so that most of the data are of low signal-to-noise (S/N) ratio. The observations consist of detections of CO in a fair number of objects, and detections of a few other molecules in a handful of objects. Because of the scarcity of data, we are not yet in a good position to evaluate from the observational point of view how the chemistry of the envelopes depends on parameters such as mass-loss rate, spectral type, or dust content.

Surveys in the CO (1-0) and (2-1) lines (e.g., Zuckerman et al., 1978; Knapp et al., 1982; Knapp and Morris, 1985) have detected CO emission in about 50 cool CS envelopes, and about half of these are carbon stars. Thus, carbon stars are strongly represented, but the significance of this has not yet been fully evaluated. Notable among the objects detected are the protoplanetary AFGL 2688 (Lo and Bechis, 1976; Zuckerman et al., 1976) and the planetary NGC 7027 (Mufson et al., 1975), whose central stars have presumably evolved from late-type carbon stars. In any event, their envelopes appear to be carbon rich (Zuckerman et al., 1976; Zuckerman, 1982). According to Knapp et al. (1982), the CO lines in many objects are optically thick and are therefore rather insensitive to the CO abundance in the envelope.  $^{13}\text{CO}$  lines have also been detected in several objects (e.g., Knapp and Chang, 1985), but they tell us more about the nuclear history of the material than its chemistry.

We give two examples of those objects which have been observed in lines other than CO. In CIT 6, HCN,  $\text{HC}_3\text{N}$ , CN, SiS,  $\text{C}_3\text{N}$ , and CS have been detected (Wilson et al., 1973; Jewell and Snyder, 1982, 1984; Allen and

Knapp, 1978; Henkel et al., 1985; Sahai et al., 1984), and in AFGL 2688, HCN,  $\text{NH}_3$ ,  $\text{HC}_3\text{N}$ ,  $\text{HC}_7\text{N}$ , SiS, CS, and  $\text{C}_2\text{H}$  have been detected (Zuckerman et al., 1976; Huggins et al., 1984a; Sahai et al., 1984; Nguyen-Q-Rieu et al., 1984b). CIT 6 (IRC + 30219) is a late-type carbon star with a mass-loss rate smaller than that of IRC + 10216 by a factor  $\sim 30$  (Morris, 1980; Knapp et al., 1982). AFGL 2688, on the other hand, is an F supergiant with a mass-loss rate comparable to that of IRC + 10216 (Morris, 1980; Knapp et al., 1982). Because lower limits on the  $^{12}\text{C}/^{13}\text{C}$  ratio in these objects are  $\sim 20$ , they may not be very different from that in IRC + 10216, where  $^{12}\text{C}/^{13}\text{C} \sim 35$ . Henkel et al. (1985) have analyzed their line observations of CIT 6 and find no significant abundance differences ( $< \text{a factor of } 5$ ) between it and IRC + 10216. Although AFGL 2688 has not been analyzed, the intensities of its molecular lines, relative to CO, are not very different from those in IRC + 10216. For these two objects, therefore, we have no strong evidence for a different chemistry. Recently, however, Beichman et al. (1983) have tentatively detected neutral atomic carbon at  $610 \mu\text{m}$  in emission in AFGL 2688, but not in CIT 6 or IRC + 10216. Their observations suggest that AFGL 2688 is very carbon rich, although the effect on the envelope chemistry of the early spectral type of the central star has not been investigated in detail. Obviously, many more sensitive observations of carbon stars, other than IRC + 10216, are needed to clarify the general characteristics of the chemistry of their envelopes as a group.

**M and S Stars.** The list of heavy molecules detected in the expanding CS envelopes of M and S stars is limited to OH,  $\text{H}_2\text{O}$ , SiO, CO,  $\text{H}_2\text{S}$ , HCN, and  $\text{NH}_3$ . There is no equivalent to IRC + 10216, showing a rich oxygen-dominated chemistry. The overall picture of the chemistry in these envelopes is therefore very incomplete.

The most extensive observations have, of course, been made in the masing transitions of OH,  $\text{H}_2\text{O}$ , and SiO. Many of these data have been tabulated by Engels (1979), and interpreta-

tions of the masing lines in circumstellar envelopes have been reviewed by Goldreich (1980) and Elitzur (1982). As yet, these observations appear to reveal little about chemical processes as such, other than that these species are present at sufficient column densities to produce the maser gain. Further general comment, therefore, is beyond the scope of this review. However, we note that the Type II OH masers may be fairly directly linked to the chemistry of the outer envelopes. Both mapping (e.g., Bowers et al., 1983) and phase-lag measurements (e.g., Herman and Habing, 1981) show that the maser emission arises in a shell of radius  $\sim 10^{16}$  to  $10^{17}$  cm. Inside this shell in optically opaque envelopes, OH is expected to be rapidly converted to  $\text{H}_2\text{O}$  by reactions with  $\text{H}_2$ , so that the presence of the OH emission requires a source of production for the radical, as discussed by Goldreich and Scoville (1976). One possibility which they suggest is the photodestruction of  $\text{H}_2\text{O}$  by ambient galactic UV photons, and further studies of this effect have been made by Deguchi (1982) and Huggins and Glassgold (1982b). The calculated sizes of the photoproduced OH shells are consistent with the observations, but they do not rule out the possibility that the OH is primarily produced by other processes.

In addition to the masers, "thermal" millimeter emission from SiO and CO has been surveyed in a number of stars (e.g., Morris et al., 1979; Zuckerman et al., 1977, 1978; Knapp et al., 1982; Knapp and Morris, 1985). HCN emission has been detected in only two S stars (Olofsson et al., 1982b), and  $\text{H}_2\text{S}$  in only OH 231.8 + 4.2 (Ukita and Morris, 1983). CO and  $\text{NH}_3$  have been observed in a handful of stars in absorption in the IR (Bernat et al., 1979; Bernat, 1981; McLaren and Betz, 1980), and low temperature (600 K) SiO absorption has been observed in VY CMa (Geballe et al., 1979). OH and  $\text{H}_2\text{O}$  have been detected in the IR in R Leo (Hinkle and Barnes, 1979), although these appear to be kinematically associated with the upper photosphere, or inner shell, rather than with the extended envelope. One

important result from the IR CO measurements is the existence of multiple velocity components, which may indicate that the mass loss is episodic (Bernat, 1981).

Specific inferences on the chemistry, based on the observations, are few. Zuckerman (1980) notes that millimeter SiS emission is not detected, implying  $\text{SiS}/\text{SiO} < 1$ , as might be expected on the basis of simple thermodynamic freeze-out in an oxygen-rich environment. Morris et al. (1979) note that, relative to CO, the thermal SiO emission is more readily observable in M and S stars than in C stars. (SiO is not detected in C stars except for IRC + 10216.) They interpret this as an abundance effect, which again is consistent with simple ideas on the different (O or C dominated) chemistries involved. However, when the SiO emission-line data are interpreted with the radiative-transfer models of Morris and Alcock (1979), Si is found to be heavily depleted ( $\sim 99$  percent) into grains in the regions sampled by the observations. As Zuckerman (1980) points out, this is unlikely to be the case in the inner regions where the SiO masers are produced, so that the bulk of the Si is condensed into grains between  $r \approx 10^{14}$  and  $10^{16}$  cm, which is at least consistent with the overall picture determined from observations of the dust.

Finally, note that the CO (2-1) observations (Knapp et al., 1980) and the KI scattering data (see below) of  $\alpha$  Ori have been modeled in some detail by Jura and Morris (1981). They find that the small size of the CO-emitting region requires that CO is photodissociated at a relatively high rate between  $10^{16}$  and  $10^{17}$  cm from the star. They also find that CO is underabundant by a factor  $\sim 25$ , relative to solar abundances fully associated, and they suggest that C is deficient by this factor in  $\alpha$  Ori. On the other hand, CO may not be fully associated. Model analysis of the CO emission in R Cas by Morris (1980) also indicates that only 10 percent of C is in CO, assuming solar abundances. Clearly, accurate CNO photospheric abundances would be very useful in refining the interpretation of observations of the circumstellar material.

## Heavy Atoms

Observations of neutral atoms and ions are potentially useful in assessing the physical conditions in CS envelopes (e.g., the degree of ionization and the degree of depletion into grains); they may also play a critical role in the buildup of molecules in the inner envelope, particularly in the presence of a warm chromosphere (e.g., Clegg et al., 1983a). It is also worth remembering that atoms and ions are the likely ultimate fate of all gas-phase circumstellar material (Huggins and Glassgold, 1982a), although they reach this state in very rarefied conditions of low column density and are difficult to detect.

A number of studies of optical circumstellar atomic lines have been made, mainly for earlier M giants and supergiants (cf. Hagen et al., 1983, and references therein; Goldberg, this volume). Lines of neutral and singly ionized metals are seen in absorption against the stellar continuum and are blue-shifted relative to photospheric lines. Analysis of the lines yields column densities, although the inner radius of the actual column observed has been a point of some controversy (see, for example, the review by Castor, 1981). Most metals observed appear to be predominantly singly ionized. According to Hagen et al. (1983), there appears to be no correlation between the quantities of circumstellar dust and atomic gas, although for the thicker envelopes of cooler stars, it is evident from the CO surveys that there is some correlation between dust and molecular gas (e.g., Knapp, 1985). In  $\alpha$  Ori, the atomic envelope has also been observed in the scattered radiation of the KI  $\lambda$  7699 resonance line. The emission has been imaged by Honeycutt et al. (1980) and Maun et al. (1984). It extends out to a radius of at least 60" and is roughly circularly symmetric. Honeycutt et al. infer a radial power law dependence for  $n(\text{KI})$  of slope  $1.65 \pm 0.2$ , and Maun et al. quote  $2.5 \pm 0.8$ ; both measurements are consistent with an inverse square power law. In principle, this information could be combined with the column density measurements of  $\alpha$  Ori to constrain detailed models of the atomic envelope, but this has not

yet been done. Because atomic column densities have been measured in  $\alpha$  Ori and several other stars with molecular envelopes, the potential exists for developing a coherent understanding of these envelopes which include all components. (See the section *Photochemistry*.)

## Other Observations

Although this discussion has emphasized observations of the extended expanding envelopes, the physical structure of the transition region between the photosphere and the extended envelope can affect, and may dominate, the chemistry of the wind flow. We comment briefly on two factors: chromospheres and shocks.

At least some cool giants and supergiants possess warm chromospheres, as evidenced by atomic emission lines and radio continuum emission. (See Querci and de la Reza, this volume.) The chromospheres can influence the outer envelope in at least two ways. First, the UV emission may dominate that of the central star and produce a substantial radiation field in the extended envelope. For  $\alpha$  Ori, for example, the UV flux has been measured, and Clegg et al. (1983a) calculated photodestruction rates for a number of molecules and neutral atoms. At 2 stellar radii, these rates are typically  $10^6$  faster than in the general interstellar medium, so that chromospheric radiation will dominate photoprocesses throughout much of the expanding envelope.

A second effect of chromospheres is that they will change the inner boundary conditions of the extended flow. Instead of the high densities, low temperatures, and low-ionization characteristic of photospheres, the physical conditions will be completely different and should affect the processes of molecular association. Unfortunately, as yet, the observations tell us little about the structure of the outer chromosphere and the inner wind flow.

Another complication in the transition region is the observed presence of shock waves. We briefly mention two striking examples. The first concerns the late-type carbon star, CIT 6,

which Cohen (1980) has observed over a period of a few years. (See the section *Heavy Molecules*.) During that time, an optical emission-line spectrum of H, O I, O II, N II, and S II developed and then vanished, which Cohen interpreted as a shock spectrum produced in regions in which recent stellar mass loss encountered the extended envelope. Associated changes in the continuum are attributed to thermal emission from dust grains which may have condensed from gas ejected during this phase. The second example concerns the S-type Mira variable,  $\chi$  Cygni, which has been extensively monitored in the IR by Hinkle et al. (1982). They find four distinct kinematic components in the CO absorption spectrum: a pulsating photosphere, a stationary 800 K shell (which they estimate to be at 10 stellar radii), an infalling component, and an outer expanding shell. Their overall picture is one in which shock waves driven through the photosphere build up the stationary layer, which in turn is the reservoir for both the expanding shell and the infalling material. These observations are a sober reminder that the physical conditions—and thereby the chemical processes—which take place in the inner regions of circumstellar envelopes may be quite complex.

## CHEMISTRY

### Time-Scale Considerations

An intrinsic difficulty in the theoretical study of CS envelopes is that the material lost by the star is carried through regions with widely differing physical conditions, beginning with both high density and temperature in the photosphere and ending with rarefied cool conditions in the far outer envelope. In between, several dynamical, thermal, and chemical processes are operative which would have to be treated self-consistently in order to have a proper theory of the mass loss and the associated properties of the CS envelope. The demand that a broad range of physical phenomena be included makes the theory of the enve-

lopes challenging as well as interesting. In fact, nothing like a comprehensive theory has been attempted thus far, in part because we do not understand enough about such fundamental problems as the mechanisms for mass loss and the formation of dust. Nevertheless, some useful first steps have been made by investigating simple but general models, such as the thermal equilibrium and the photochemical models discussed below.

At this early stage in the theoretical study of CS chemistry, it has been customary to make several simplifying assumptions which serve to isolate the chemistry from other problems. In particular, one or more of the following distributions are specified a priori: density, velocity, temperature, and dust. For example, in the following, the discussion is restricted to spherically symmetric and steady flows, with the gas density following an inverse square law at large distances, as described by Equation (6-1). Likewise, with a few notable exceptions, dust and temperature profiles have been specified rather than calculated consistently together with the chemistry. Whenever possible, these distributions are based on observational information, which is rather limited at this stage.

The chemistry of CS envelopes is basically time-dependent; this follows from their small size ( $< 1$  pc). Most chemical time scales will become larger than the dynamical time scale somewhere in the shell. We use the following definition for the dynamical time scale (always measured in seconds),

$$\tau_{dy} = r/v = 1 \times 10^9 \left( \frac{r_{15}}{v_6} \right), \quad (6-4)$$

where  $r$  and  $v$  are measured in units of  $10^{15}$  cm and  $10^6$  cm s $^{-1}$ . For typical inner and outer radii of  $10^{15}$  and  $10^{17}$  cm and an expansion velocity of 10 km s $^{-1}$ , the dynamical time scale ranges from  $10^9$  to  $10^{11}$  s, or 30 to 3000 yr.

A qualitative understanding of the time-dependent nature of CS chemistry is aided by classifying reactions as one-body, two-body,

three-body, etc., according to the number  $p$  of reactants. Important examples for CS shells are:

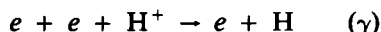
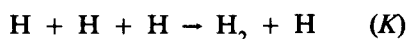
1. Photo processes—For example,



2. Ordinary chemical reactions—For example,



3. Three-body reactions—For example,



The symbols in parentheses are generic rate constants. This classification is significant because the various types have very different rate constants and time scales. If we use:

$$\tau_{ch}(X) = n(X) / \frac{dn(X)}{dt}$$

as the definition of the chemical time scale for species  $X$ ,  $\tau_{ch}(X)$  will be proportional to  $r^{2(p-1)}$ . To illustrate, some examples are:

1. Photo time scale:

$$\tau_{ph} = \left[ G_{IS} J(r) + G_0 K(r) \left( \frac{R_0}{r} \right)^2 \right]^{-1} \quad (6-5)$$

Here,  $G_{IS}$  is the asymptotic rate at the outside of the shell due to interstellar radiation,  $J(r)$  is the shell attenuation factor to be discussed in the section *Photochemistry*,  $G_0$  specifies the rate due to stellar or CS (e.g., chromospheric) radiation specified at some nominal distance

$R_0$ , and  $K(r)$  gives corrections to the inverse square dilution factor, including attenuation by the shell. A characteristic value for  $G_{IS}$  is  $1 \times 10^{-10} \text{ s}^{-1}$ , so that photodestruction times in the farthest outer envelope are of the order of 100 yr.  $\alpha$  Ori is an example of a star with a strong UV field, and  $G_0$  is about  $10^6 \times G_{IS}$  at  $R_0 = 1(14) \text{ cm}$ ; thus, photodestruction by chromospheric radiation dominates its CS shell out to  $> 3 \times 10^{17} \text{ cm}$ .

2. Two-body chemical time scale:

$$\tau_{ch} = 333 r_{15}^2 e^{T^*/T} \frac{\dot{M}_{-5}}{V_6} \quad (6-6)$$

$$\times \begin{cases} 1/x' & \text{for destruction,} \\ x/x'x'' & \text{for formation.} \end{cases}$$

The reactant abundances have been denoted by  $x$ ,  $x'$ , and  $x''$ , with  $x$  for the species whose time scale is of interest and  $x'$  and  $x''$  for other species. The rate constant for the exothermic direction has been written as  $k = A \exp(-T^*/T)$ , where the preexponential factor usually depends weakly on temperature  $T$ . The numerical value used in Equation (6-6),  $A = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , is for a relatively fast neutral reaction. There are three critical factors in this formula:

- a. Expansion of the shell—The  $r^2$  effect alone boosts the numerical factor to 25 yr at  $3 \times 10^{17} \text{ cm}$ .
- b. Activation energy—If  $T^*$  is large, the exponential makes the chemical time scale much larger than all others in the cool outer envelope (i.e., exothermic reactions with large activation energies are readily frozen out). Clearly, endothermic reactions will also be frozen out when  $T$  becomes much less than

$G/K_B$ , where  $G$  is the free energy of the reaction.

- c. Abundances—The factors  $1/x'$  for destruction and  $x/x'x''$  for production can also increase the time scale significantly.

Despite these obstacles, the moderately high temperatures in the dense inner regions of CS envelopes provide conditions for chemical activity which are not found in cool molecular clouds.

### 3. Three-body time scale:

As examples, we give the time scales for the recombination of three H atoms:

$$\tau(\text{H}_2) = 8.3 \times 10^{13} \text{ s } T^{3/4} r_{15}^4 \left( \frac{V_6^2}{\dot{M}_{-5}^2} \right), \quad (6-7)$$

and the time scale for three-body recombination of  $\text{H}^+$  with two electrons:

$$\tau(\text{H}^+) \cong 10^{12} \text{ s } \frac{T r_{15}^2}{x_e^2} \left( \frac{V_6^2}{\dot{M}_{-5}^2} \right). \quad (6-8)$$

The additional factor of  $r^2$  means that three-body reactions are only important close to the star.

The implications of the above time-scale estimates will be discussed below in the context of specific models and objects. In general, they span a large range of values, depending on the abundances and the activation energies entering into individual reactions. At this stage, it is sufficient to note, for example, that the chemical time scales will be longer than the dynamical time scales at large distances, and that photo time scales can dominate in different parts of the envelope, depending on the radia-

tion source (stellar or interstellar) and dilution and attenuation effects. Therefore, the chemistry of CS envelopes is essentially kinetic in character, rather than steady state.

## Thermal Equilibrium Models

Thermal equilibrium represents the simplest of all models because the results depend only on temperature, pressure, and elemental abundances—and not at all on the specifics of reaction mechanisms. Underlying the model is the assumption that the conditions for equilibrium are met (i.e., that all the relevant reactions are in detailed balance). Although these conditions may be expected to be satisfied inside the star, they will eventually fail as the temperature and density decrease going away from the star.

As we have seen in the section *Time-Scale Considerations*,  $\tau_{ch} \ll \tau_{dy}$  for small  $r$  and  $\tau_{ch} \gg \tau_{dy}$  for large  $r$ . Thus, a freeze-out position  $R_{FO}$  can be defined by the condition that  $\tau_{ch} = \tau_{dy}$ ;  $R_{FO}$  depends sensitively on species. Less reactive species (e.g.,  $\text{H}_2$  and CO) may freeze out close to the star, whereas radicals may not freeze out until well into the envelope. Most applications of the thermal equilibrium model have been based on the premise that a *single* freeze-out location applies to all species, in contrast to the more realistic situation in which each species freezes out at a different place.

A basic limitation in applying the thermal equilibrium model is the quality of the thermochemical data. For IRC + 10216, for example, the data required to calculate the abundances for the most complicated and exotic species do not exist.

Early comparisons of observations of CS molecules in IRC + 10216 with thermal equilibrium calculations were made by Morris (1975), Ridgway et al. (1976), and Hall and Ridgway (1978). The last authors, for example, found that the relative column densities of CO,  $\text{C}_2\text{H}_2$ , HCN and  $\text{CH}_4$  could be accounted for by a C-rich supergiant atmosphere with  $T \cong 1000 \text{ K}$  and  $n \cong 1 \times 10^{14} \text{ cm}^{-3}$ . A more comprehensive application of the model to this same object was made by McCabe et al. (1979),

who did equilibrium calculations both with and without graphite formation. These authors compiled abundances of a dozen CS molecules and radicals from available observations, and they attempted to find a single set of temperature and pressure values which would give the best agreement between the thermal equilibrium model and the observations. Their best-fit parameters were  $T \cong 1250$  K and  $n \cong 4 \times 10^{14}$  cm $^{-3}$  and required the omission of dust formation. They obtained a factor of 2 to 5 agreement for eight molecules (relative to CO), but four others were in serious disagreement (3 to 6 orders of magnitude): CN and NH $_3$  were observed to be greatly overabundant, and SiO and SiS were greatly underabundant. The very large pressure adopted for the upper atmosphere of IRC + 10216 seems to be inconsistent with our present understanding of the upper atmospheres of cool stars.

Thermal equilibrium calculations for IRC + 10216 have been repeated by Lafont et al. (1982), with improved estimates of abundances and thermochemical data. They used a broader criterion for agreement (a factor of 10), consistent with the large uncertainties in these quantities, and they worked with lower pressures. However, their overall results are similar to those of McCabe et al. (1979). Figure 6-1 gives an example of their results for C/O = 2.

We can summarize the equilibrium model for IRC + 10216 using the rough abundances given in Table 6-1 and the equilibrium calculations discussed above:

1. The simplest C,N,O molecules and hydrocarbons:
  - a. The model works well for CO, C $_2$ H $_2$ , HCN, and CH $_4$ .
  - b. The model fails for NH $_3$ , which is observed to be overabundant by a large factor.
2. Sulfur and silicon molecules:
  - a. CS is somewhat overabundant.

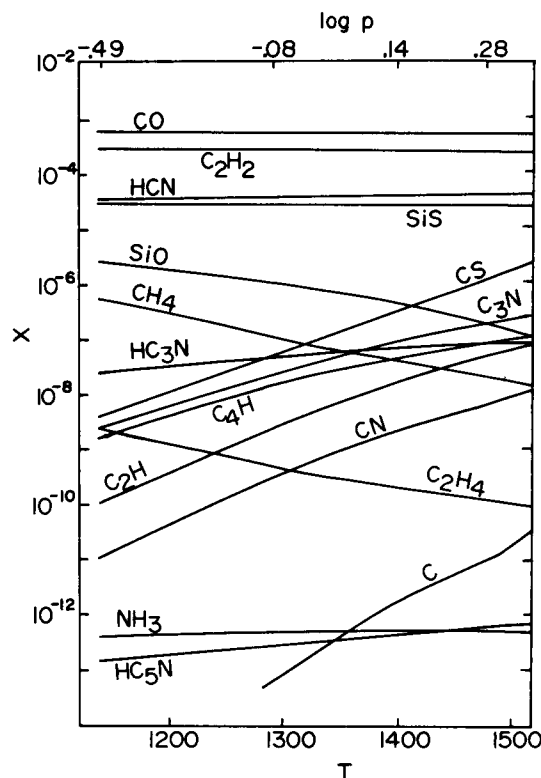


Figure 6.1. Thermal equilibrium abundances calculated for the envelope of IRC + 10216 by Lafont et al. (1982) assuming C/O = 2.

- b. SiS and SiO are underabundant by very large factors.
3. Chain molecules:
  - a. HC $_3$ N agreement is satisfactory, but HC $_5$ N is grossly overabundant.
  - b. The thermochemical data base is too weak to make definitive conclusions on the other cyanopolyynes and related species.
4. Radicals:
  - a. All radicals are overabundant by large factors.
  - b. The worst cases are CN and C $_2$ H.

Another way of stating item 4 is that the ratios of radicals to parent molecules (i.e., CN/HCN,  $C_2H/C_2H_2$ , and  $C_3H/HC_3N$ ) are much larger than expected on the basis of thermal equilibrium; this suggests that the radicals are made by some process directly from their parents. In conclusion, we find that the simple thermal equilibrium model (unique choices for  $T$  and  $p$ ) is consistent with the measured abundances of only the few most abundant molecules.

Even the limited successes of the thermal equilibrium model must be viewed with some skepticism as long as dust formation has been omitted from the calculations. Although the most abundant molecules may be frozen out in the upper atmosphere, as suggested by the above fits, some of them may participate in the formation of dust. Otherwise, it is unlikely that the envelopes would be as dusty as they are. Certainly, the time scale for a gas molecule to strike a dust grain, Equation (6-10) below, is less than the dynamical time scale in the relevant regions, roughly from  $10^{14}$  to  $10^{15}$  cm. As our knowledge of the thermochemical quantities improves, it would be of interest to develop the equilibrium model further to include the formation of dust, as well as more complicated molecules.

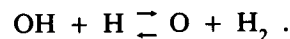
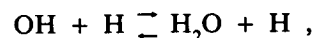
The distribution of atomic and molecular hydrogen in the upper atmospheres of cool stars can be studied in detail because the relevant reactions are limited and are fairly well understood (Glassgold and Huggins, 1983). As discussed in the section *Observations*, molecular hydrogen has been detected in very cool stars, but all attempts to detect the 21-cm line of atomic hydrogen have been unsuccessful thus far. Molecular hydrogen is a good example of a molecule which freezes out close to the photosphere. Figure 6-2 shows the fraction of atomic hydrogen obtained from equilibrium calculations in which  $T$  and  $p$  profiles were specified by model atmosphere calculations (Johnson et al., 1975; Lucy, 1976; the latter having an expanding wind). The variation in the physical conditions in the upper stellar atmo-

sphere changes the  $H/H_2$  ratio by large amounts. The open circles in the figure indicate where freeze-out of three-body recombination occurs according to the time-scale estimate (Equation (6-7)). This freeze-out ratio provides the initial condition for calculating any changes which the hydrogen undergoes in the CS shell, as will be discussed in the following sections.

### Studies of Chemical Reactions

In this section, we discuss the reactions appropriate for describing the chemical evolution of CS wind material. We consider regions in which the formation of dust has essentially ceased, but do not completely ignore the chemical activity associated with dust. Photoprocesses will be discussed in the next section. It is useful to divide the discussion of CS chemistry according to whether the environment is carbon- or oxygen-rich, and we begin with O-rich stars.

Goldreich and Scoville (1976) solved the time-dependent equations for the  $H_2O$  and OH system, using only the following reactions:



They considered a  $1 M_{\odot}$  star with a mass-loss rate of  $3 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$  and a terminal velocity of  $20 \text{ km s}^{-1}$ . They found that these reactions maintained equilibrium abundances out to  $2 \times 10^{15}$  cm, (where  $T = 500 \text{ K}$  and  $n = 1 \times 10^7 \text{ cm}^{-3}$ ), beyond which they are frozen. Scalo and Slavsky (1980) made similar calculations without including shielding, but extending the chemistry to include silicon, and generally underscored the importance of time-dependent chemistry. These authors have recently completed a comprehensive study of the chemistry of O-rich CS envelopes (Slavsky and Scalo, 1984).



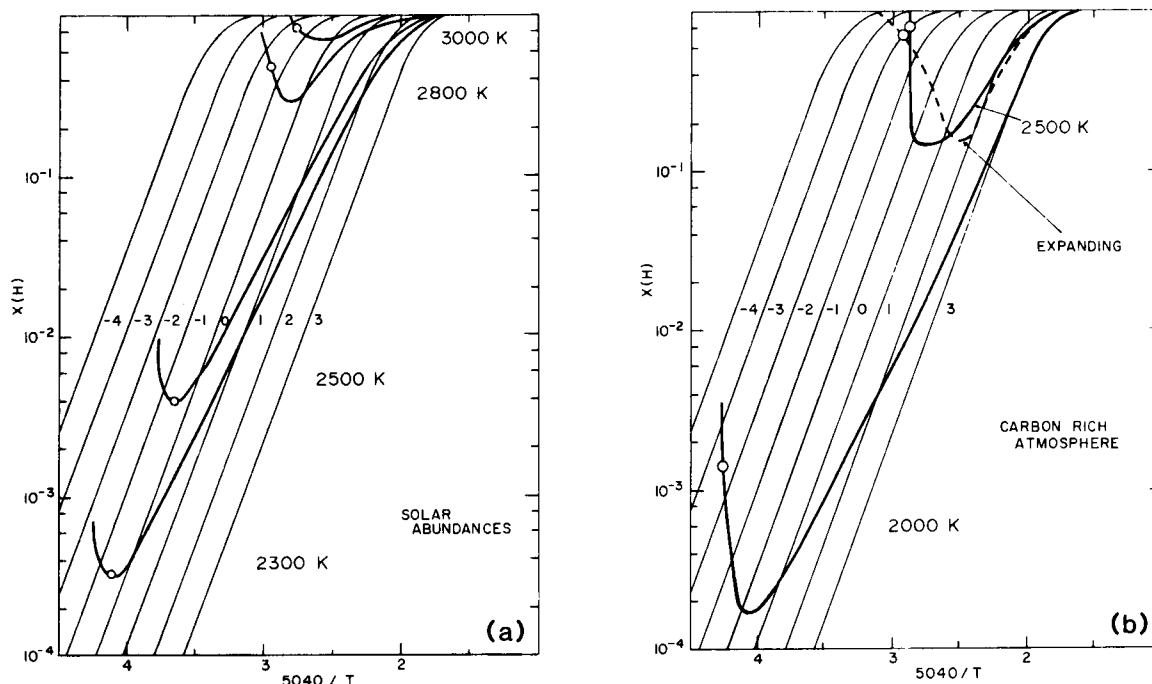


Figure 6-2. Thermal equilibrium abundance of atomic hydrogen calculated by Glassgold and Huggins (1983) for the atmospheres of (a) O-rich and (b) C-rich stars for several photospheric temperatures. The heavy lines trace the variation starting from the photosphere in the upper right; the open circles show where freeze-out occurs. The other curves are isobars labeled by  $\log p$ .

A similar position was taken by Jameson and Williams (1981), who solved a restricted system of rate equations appropriate for the study of interstellar carbon and oxygen chemistry: molecules are formed by ion-molecule reactions ( $\text{H}^-$  for  $\text{H}_2$ ), radiative association, and neutral reactions and are destroyed by ion-molecule reactions; the ions are produced by cosmic rays. The initial condition was that all species were dissociated and ionized; solar abundances were assumed. Jameson and Williams showed that this plasma quickly recombined and that substantial molecular synthesis occurred before freeze-out, depending on the initial density. Rather different abundances would have been obtained if the initial conditions had been appropriate for cool stars. On the other hand, such plasma might result from chromospheric conditions.

Clegg et al. (1983a) extended the chemical analysis of Scalo and Slavsky (1980) by including the  $\text{H}-\text{H}_2$  and the  $\text{C}^+-\text{C}-\text{CO}$  systems, as well as by incorporating reactions to describe

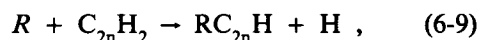
the oxygen and silicon compounds expected for O-rich envelopes. They used the density profile for an expanding wind and carried out steady-state calculations for a particular temperature profile:  $T = 1000 \text{ K}$  for  $r$  in the range 2 to  $5 R_*$ , and decreasing as  $1/r$  for  $r$  in the range 5 to  $30 R_*$  (the calculation is cut off at this point); dust formation is ignored. Solar abundances are used, and although the results are intended to apply to a variety of O-rich envelopes,  $\alpha \text{ Ori}$  is used as an example with  $R_* = 7 \times 10^{13} \text{ cm}$ ,  $\dot{M} = 2 \times 10^{-6} M_\odot \text{ yr}^{-1}$ , and  $v = 1 \text{ km s}^{-1}$ . Most important, Clegg et al. calculate the rates for photoionization and photodissociation by the chromospheric UV radiation field of  $\alpha \text{ Ori}$  for  $\text{H}^-$ , the heavy elements Mg, S, Na, and Ca, and oxygen- and silicon-bearing molecules. The rates are typically  $10^6$  larger than those familiar from the interstellar medium, and these large values are confirmed by independent calculations by Bernat (1976)

and ourselves. Such strong photodestruction greatly inhibits molecule formation, although it still occurs at a reduced level. Of course, stars without strong chromospheres will have shells which are more conducive to the formation of molecules. In the presence of a strong radiation field, the temperature profile adopted by Clegg et al. is inappropriate (i.e., chromospheric temperatures are considerably larger than 1000 K). Finally, Clegg et al. find that the use of steady abundances is justified in many cases, but an important exception is the H-H<sub>2</sub> system.

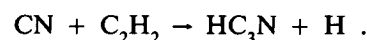
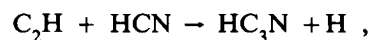
One of the most important questions relating to the silicon chemistry is the rather low abundance of SiO deduced from nonmaser microwave emission, as discussed in the section *Heavy Molecules*. Scalo and Slavsky (1980) suggested that destruction by chromospheric UV radiation might be an alternative to the more obvious explanation that the silicon is mainly condensed into dust. They assumed that silicon entered the CS shell of  $\alpha$  Ori in the form of atoms, and then showed that relatively little SiO was formed by reactions with OH (produced by photodissociation of H<sub>2</sub>O). The work of Clegg et al. (1983a) supports this, and they calculate correctly that the appropriate form for most of the gaseous silicon is Si<sup>+</sup>. Practically nothing is known about the photodissociation of SiO, and Clegg et al. estimate that the rate is the same as that of CO (which is not well understood either). The conclusion that stars with chromospheres have low SiO abundances is fairly independent of this rate; moreover, it could be tested by observations to detect chromospheric activity.

No solutions are available for systems of chemical reactions appropriate to C-rich stars. It is generally accepted, on the basis of comparing the chemical and dynamical time scales (Equations (6-4) and (6-6)), that fast reactions with small activation energies can operate far out in the shells. Certainly radicals, which are either emitted by the star or produced by photodissociation, will participate in such chemical activity—and this holds for O-rich and C-rich shells. A general survey of chemical processes

in C-rich stars has been given by Lafont et al. (1982). They pointed out that chemical reactions with radicals  $R$  of the type:

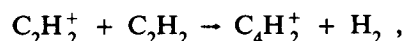


which have recently been discussed in the context of Titan's atmosphere (Allen et al., 1980), may also be relevant for CS chemistry. The measured rate constant in the case of  $R = C_2H$  and  $n = 1$  (acetylene) is large ( $k = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), and the activation energy is probably small. Reactions of this type provide the means for synthesizing acetylene and cyanoacetylene chains. For example, the following reactions could produce HC<sub>3</sub>N:

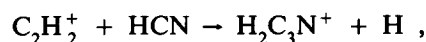


Although we are not aware of any measurement of the first reaction, the rate for the reaction of CN with acetylene into all possible channels has been measured to be  $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Schacke et al., 1977); branching to C<sub>3</sub>N is likely.

We have also analyzed some of the reactions that might be operative in C-rich CS envelopes. The ion C<sub>2</sub>H<sub>2</sub><sup>+</sup>, produced by photoionization of acetylene, may be an important progenitor of ion-molecule hydrocarbon reactions which lead to chain molecules. Two examples of reactions in which the measured rate constants are large are:



$$k = 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1},$$



$$k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

These reactions lead to C<sub>4</sub>H and HC<sub>3</sub>N by dissociative recombination of the ions with electrons. Thus, there are promising leads to investigate, but their analysis may not be simple.

First of all, important gaps exist in our information on rates for chemical reactions. Second, many species must be considered simultaneously, and the reaction network must include a good theory of the ionization of the shell. Finally, the chemistry must be formulated in terms of differential equations in order to follow the intrinsic time dependence of the chemistry.

Until now, we have focused on reactions in the gas phase. Even in regions in which the formation of dust has essentially ceased, the dust could be chemically active. Furthermore, there may be no sharp demarcation between regions with and without dust formation. In grain chemistry, the shortest time scale is that for collisions of atoms and molecules with dust particles, using the geometric cross section. We make a rough estimate using the properties of interstellar dust as determined from extinction studies and measuring grain cross sections in units of  $10^{-21} \text{ cm}^2$  (the column density  $2 \times 10^{21} \text{ cm}^{-2}$  for one magnitude of visible extinction corresponds to a cross section of  $0.5 \times 10^{-21} \text{ cm}^2$ ):

$$\tau_{gr} \simeq 3.3 \times 10^7 r_{15}^2 (U/\dot{M}_{-5} \sigma_{gr-21}) , \quad (6-10)$$

where  $U$  is the ratio of the gas expansion velocity to the gas/grain relative (or drift) velocity. For sufficiently large mass-loss rate, grain area, and relative velocity, this time scale can be smaller than the dynamical time scale in the inner part of a CS dust shell. On the other hand, Equation (6-10) indicates that any grain chemistry will freeze out in the outer envelope. (This discussion completely omits the difficult questions of the probabilities for sticking and subsequent chemical activity, whose consideration would certainly lead to time scales longer than those given by Equation (6-10).)

The collision of the gas and dust can lead to both the formation and the destruction of molecules and to the incorporation of gaseous species into the dust particles. Little is known about these processes in general, but it is almost certain that they are specific to the dust surface and incident species. Lafont et al. (1982) believe

that the most likely grain reaction is the production of  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  following the sticking of H atoms. They also suggest that radicals such as CN and  $\text{C}_2\text{H}$  are almost certain to react on striking a dust grain. A large fraction of these particular radicals may be produced, however, by photodissociation farther out in the shell where the probability for hitting a grain is negligible.

Glassgold and Huggins (1983) discussed the possibility that the warm grains in the inner envelope catalyze the formation of  $\text{H}_2$  following H chemisorption, whereas Lafont et al. (1982) consider it very unlikely that any strongly bound molecule can be synthesized on CS grains. In view of our ignorance about almost all physical and chemical properties of CS grains, the question of catalysis in the inner part of the envelope (but after the dust has already been formed) must be left open.

We conclude this discussion of chemical reactions with some remarks on shocks. Shock phenomena are common in the interstellar medium because there are many ways to generate supersonic velocities (e.g., supernova remnants, winds from young stellar objects, collisions between clouds, etc.). The shocks are important for the transfer of energy and momentum and for the emissivity and chemical composition of the interstellar gas. (See the reviews by McKee and Hollenbach, 1980; and Hollenbach, 1982.) If shocks are present in CS shells, they may play important analogous roles in affecting the physical properties of these envelopes.

Shocks in CS shells have been discussed primarily in the context of the origin of the mass loss (e.g., Willson, 1976; Willson and Hill, 1979; Wood, 1979). In these calculations, stellar pulsations drive shocks into the atmosphere, which leads to mass loss. The observational evidence for shocks in  $\chi$  Cygni obtained by Hinkle et al. (1982) supports this general picture. However, there have been no theoretical studies of the thermal and chemical effects of shocks propagating through CS envelopes. Judging from the theory of interstellar shocks, we might

expect that the resulting enhancements in density and temperature would promote both chemical activity and the excitation of characteristic line radiation—potentially useful for diagnostic purposes. Very likely the ratio of radicals to parent molecules would be enhanced. The detailed predictions should depend on the velocity of the shock and on the density of the ambient shell (i.e., on mass-loss rate). Calculations of shocks in CS shells should prove to be quite illuminating.

### Photochemistry

Photodestruction is important because it significantly affects the chemical composition of the CS wind. The radiation may be either external (e.g., the interstellar radiation field) or from the star itself. Most of this section will deal with the first situation; some effects of chromospheric radiation have already been mentioned in the foregoing section, *Studies of Chemical Reactions*.

The photodestruction process for a species in an expanding wind can be characterized by two parameters, the mean distance it travels (ignoring absorption) before being destroyed by radiation,  $V\tau_{ph}$ , and the absorption length,  $d$ . The simplest case is the ambient interstellar radiation field, where  $\tau_{ph} = 1/G_{IS}$ . Because  $G_{IS}$  ranges from  $10^{-11}$  to  $10^{-9} \text{ s}^{-1}$ , molecules which are easily destroyed by radiation would survive only to  $10^{15} \text{ cm}$  in an unshielded shell, whereas molecules which are difficult to destroy would survive out to  $\sim 10^{17} \text{ cm}$ . The radial dependence of the abundance is  $\exp(-rG_{IS}/V)$ , but when shielding is present, the molecules survive longer and the radial dependence for thick shells becomes  $\exp(-d/r)$ . The shielding distance,  $d$ , depends on the molecule in question because the cross sections for dissociation and absorption are sensitive functions of wavelength.

These qualitative considerations have been investigated by solving rate equations appropriate for an expanding envelope. For a species,  $X$ , with abundance relative to the total density

of hydrogen  $x = n(X)/n$ , the equation in a co-moving frame is:

$$\frac{\partial}{\partial t} x = -G(r(t))x + P(r(t)) \quad , \quad (6-11)$$

where  $r(t)$  locates a fluid element at time  $t$  (i.e.,  $\dot{r}(t) = v(r(t))$  where  $v(r)$  is the specified velocity profile), and  $G$  and  $P$  are destruction and production rates. The simplest example is the solution for the case  $P = 0$  and destruction by interstellar radiation is shielded exponentially. That is,

$$G(r) = J(r)G_{IS} \quad , \quad (6-12)$$

$$J(r) = \exp(-d/r) \quad . \quad (6-13)$$

The exact solution (Huggins and Glassgold, 1982a) for constant  $v = V$  is:

$$x(r) = x_0 [\exp(-rG_{IS}/V) E_2(d/r)] \quad , \quad (6-14)$$

where  $E_2$  is a standard exponential integral. It has also been possible to obtain an exact solution for a "photodissociation chain," at which the products of photodissociation are themselves destroyed by radiation (e.g.,  $\text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} \rightarrow \text{C}_2 \rightarrow \text{C} \rightarrow \text{C}^+$ ); Figure 6-3 shows this chain as calculated for IRC + 10216. The solution (Equation (6-14)) was obtained independently by Jura and Morris (1981), using a different technique.

From the above discussion, we see that the radial distributions of progenitor and fragment species are determined by the "free" photodissociation rates for a given radiation field, such as the mean interstellar field, and by the optical properties of CS material at wavelengths at which the CS species are destroyed by radiation. It is therefore important to discuss how well these quantities are known before applying the photochemical model to observations of CS shells.

Reasonably good information is available on the photodissociation cross sections for the

most stable molecules injected into CS envelopes (e.g.,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ , and  $\text{CH}_4$ ); two notable exceptions are  $\text{CO}$  and  $\text{SiO}$ . Improved far-UV absorption cross sections have recently become available for  $\text{CO}$  through the use of synchrotron radiation sources, and it seems likely that, with new instrumentation, better information on the photodissociation process will become available in the next few years. Of course, much less is known about radicals, but here the level of theoretical effort has been increasing. It should be noted that great accuracy is not required in considerations of CS photochemistry, especially for the products of molecular breakup. Certainly, at this stage we have the essential information, which is the relative values of the important rates. Thus, our position is that the unshielded rates can be considered as known relative to other uncertainties in the problem.

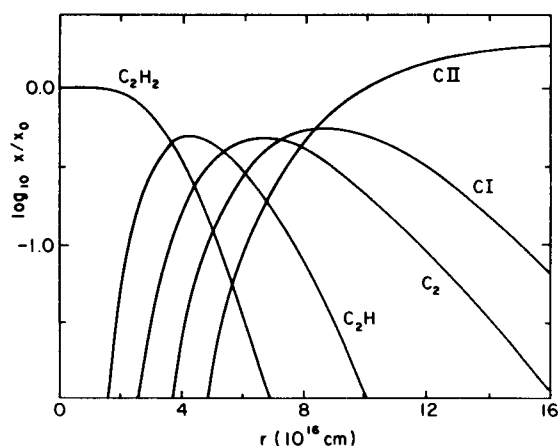


Figure 6.3. The  $\text{C}_2\text{H}_2$  photodestruction chain calculated for envelope parameters typical of IRC + 10216 (Huggins and Glassgold, 1982a).

The situation with regard to the optical properties of CS material is just the opposite. Here, dust grains play an important role, and we know essentially nothing about the far-UV extinction and albedo of CS dust. For certain species (e.g.,  $\text{CO}$ ,  $\text{C}$ , and  $\text{S}$ ), the wavelength region below  $1100 \text{ \AA}$  is critical. We conclude that determining the optical properties of the CS

dust becomes one of the objectives of studying the spatial distribution of the molecules. In order to progress, we must begin with some model for the dust, and our initial choice has been to assume that the CS dust has the same optical properties as interstellar dust. The status of this first-order assumption will be discussed below in the context of IRC + 10216 (see also Lefèvre, this volume, and Sopka et al., 1985).

The far-UV radiation is absorbed in the envelope by atoms and molecules with large absorption cross sections and abundances (i.e.,  $\text{H}_2$ ,  $\text{C}$ ,  $\text{CO}$  (and  $\text{H}_2\text{O}$  for O-rich shells)), as well as by dust. Although a detailed discussion of these shielding problems would be inappropriate here, they do have a quantitative effect on molecular distributions, as will be discussed below for the case of  $\text{CO}$ .

When the optical properties and spatial distribution of all the absorbers have been specified, the attenuation factor in Equation (6-12) must be calculated by solving the equation of transfer. At this stage, it is appropriate to use approximate solutions (e.g., the closed forms given by Gerola and Glassgold, 1978). If dust attenuation dominates, this approximation reduces to the simple exponential form, Equation (6-13), for thick shells with the shielding length given by

$$d = C/N_{sh} \quad (6-15)$$

Here  $N_{sh}$  is the column density of hydrogen which produces unit optical depth (assuming the same dust-to-gas ratio as the interstellar medium), and  $C$  is the parameter which specified the density in Equation (6-2). This length depends on species; for  $\text{CO}$ ,  $d = 6 \times 10^{16} \text{ cm } \dot{M}_{-5}/V_6$ .

The case of  $\text{CO}$  deserves special mention. First, recall that dust can provide substantial shielding of  $\text{CO}$ . Using Equations (6-13) and (6-15), we can express the attenuation factor as:

$$J(r) = \exp [-N_{sh}/N(r)] \quad (6-16)$$

where the outside column density,  $N(r) = C/r$ , is measured from infinity to position  $r$ ; in this

case,  $N_{sh} = 5 \times 10^{20} \text{ cm}^{-2}$ . There are two kinds of self-shielding to consider, depending on whether CO photodissociation proceeds by way of line absorption followed by breakup or whether it is directly dissociated with a smoothly varying cross section. Until recently, continuum dissociation was believed to dominate, in which case Equation (6-16) would still apply, but  $N_{sh}$  would be replaced by a constant times  $N(\text{CO})$ , the column density of CO. This has the effect of steepening the rise in the CO abundance going into the envelope, because  $\chi(\text{CO})$  is proportional to  $1/J$ . We also see that self-shielding introduces a nonlinearity into the calculation of the abundance of CO. If CO photodissociation is basically a line process, which seems likely (Glassgold et al., 1985), then the CO abundance curve is changed for the cross section, assumes larger values than in the continuum case, and the radiation transport is modified. Figure 6-4 (from Morris and Jura, 1983a) shows how the different kinds of shielding operate on the CO density profile for IRC + 10216. Curves C and N refer to no dissociation (constant abundance) and no shielding, respectively; the intermediate cases are D for dust only and  $n = 2, 5$ , and 10 lines producing self-shielding. Morris and Jura suggested that the large spatial extent of CO in IRC + 10216 might be explained by line self-shielding.

In the recent calculations with the photochemical model, recombination of ions has been included, as well as photoprocesses. For example,  $\text{C}^+$  is the eventual dominant form of carbon toward the outside of the shell, just as in the interstellar medium. In order to obtain a quantitatively correct treatment of the transition from C to  $\text{C}^+$  and to obtain the proper asymptotic  $\text{C}/\text{C}^+$  ratio, recombination must be included. The other situation in which recombination is important is that in which molecular ions are produced by photoionization (i.e., both  $\text{C}_2\text{H}_2^+$  and  $\text{C}_2\text{H}$  are obtained when UV photons are absorbed by acetylene). In such cases, dissociative recombination into various radicals occurs rapidly, and it is sufficient to reexpress this sequence in terms of renormalized photo rates (Huggins and Glassgold, 1982a).

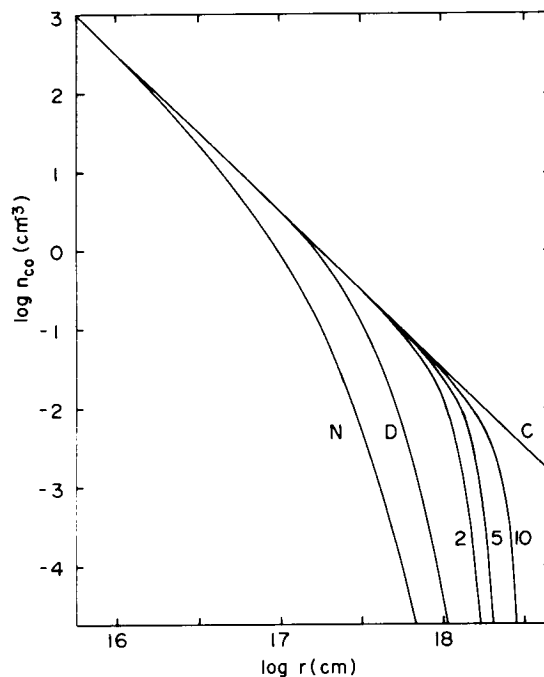


Figure 6-4. The effect of shielding on the CO density in the envelope of IRC + 10216 (Morris and Jura, 1983a). Curves C and N refer to no dissociation (constant abundance) and no shielding, respectively; the intermediate cases are D for dust only and  $n = 2, 5, 10$  lines producing self-shielding.

The photodestruction of molecular hydrogen in CS envelopes has been discussed by Zuckerman et al. (1980) and Morris and Jura (1983a), as well as by Glassgold and Huggins (1983), whose treatment we follow here. As discussed in the sections *Thermal Equilibrium Models* and *Studies of Chemical Reactions*, the chemical evolution of the  $\text{H}/\text{H}_2$  ratio can be traced from the photosphere to the outer envelope. If there is no warm grain formation of  $\text{H}_2$  in the inner envelope, this ratio is determined by freeze-out in the upper atmosphere of the star. Present stellar atmospheres suggest that, for stars with  $T_* > 2500 \text{ K}$ , the frozen outflowing hydrogen will be mainly atomic. For cooler stars, the question then becomes how much of the atomic H in the outer envelope is due to the low level initially frozen out and how much arises from that photodissociation. A

small amount of H is also produced by the photodestruction of the most abundant hydrocarbons in C-rich envelopes (Lafont et al., 1982) and from H<sub>2</sub>O for O-rich shells.

The radial distribution of H has been derived from a time-dependent theory of H<sub>2</sub> photodissociation (by way of the Lyman band lines) appropriate for an expanding shell with dust. In the interior of the shell, the solution is similar to that given for heavy molecules in Equation (6-14). That is,

$$f(r) = f(R_0) \times \exp(-a[E_{3/2}(d/r) - E_{3/2}(d/R)]) \quad (6-17)$$

where  $a = (d G_{JS}(H_2)/V) [dM/C]^{1/2}$  and  $M = 6.7 \times 10^{11} \text{ cm}^{-2}$ . For  $r \gg d$ , the exponential in Equation (6-16) varies as  $r^{3/2}$ . At the edge of the shell, there is a very sharp transition to complete dissociation. The spatial distribution of atomic H is illustrated in Figure 6-5, for which the initial value was assumed to be zero.

We complete this discussion of CS photochemistry with some examples. We first consider the heavy molecules in the C-rich envelope, IRC + 10216. We begin with the idea that IRC + 10216 has no strong internal source of UV radiation, or if it does, it is well shielded from the bulk of the envelope. We use observations to specify the most abundant species entering the outer envelope and consider how they are altered by photoprocesses initiated by UV radiation penetrating from the outside. The remaining species will be similarly modified, but other chemical processes will also be important in these cases.

We consider those radicals (e.g., CN and C<sub>2</sub>H) whose observed abundances are not reduced much from their likely progenitors (HCN and C<sub>2</sub>H<sub>2</sub>, respectively). Because both progenitors are observed to be abundant in the inner envelope (from IR absorption measurements), it is natural to investigate whether the radicals can be the result of photoproduction. This question can be pursued in some detail for

the HCN-CN system because both species have been well observed in IRC + 10216. For C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H, the data are less extensive, and additional processes (e.g. reactions involving C<sub>2</sub>H<sub>2</sub><sup>+</sup> as mentioned in the section *Studies of Chemical Reactions*) may be operative.

The photochemical model has been applied to IRC + 10216 by a number of authors, including Wootten et al. (1982) and Jura (1983a) in the context of the HCN-CN problem and by Huggins et al. (1984b) for both the CN and C<sub>2</sub>H problems. Figure 6-6 shows the CN  $N = 1-0$  and  $N = 2-1$  line shapes for the Kitt Peak (66") and Owens Valley (30") beams, as calculated by the last authors. The symbol C indicates calculations for the best fit to the 1-0 peak line intensity observed with the Kitt Peak beam, using a *constant* abundance of 1.3(-6). Curves with S are based on the photochemical model and thus have variable HCN and CN abundances; S stands for standard (interstellar) dust, whereas S/3 and SX3 stand for dust which gives three times less and three times more extinction. Equally acceptable fits to the 1-0 data can be obtained with both the constant and photoproduction models, but the constant abundance model fails to fit the roughly flat-topped 2 K line observed at Owens Valley. The 70" map size observed at Owens Valley cannot be explained by a constant abundance, but a variable abundance model with an opacity 1 to 3 times standard agrees with all of the measurements.

A similar conclusion about the dust in IRC + 10216 was reached by Jura (1983a) by applying the photochemical model to the spatial distribution of HCN as measured by Olofsson et al. (1982a) and Welch et al. (1981). Thus, the observed properties of the HCN-CN system in IRC + 10216 are consistent with the photochemical model. The more limited information on C<sub>2</sub>H can be reproduced by either a constant or variable abundance model. The above discussion suggests that important information can be obtained about CS dust by detailed fitting with the photochemical model. High-resolution studies of CS shells are also seen to be required to provide useful comparisons.

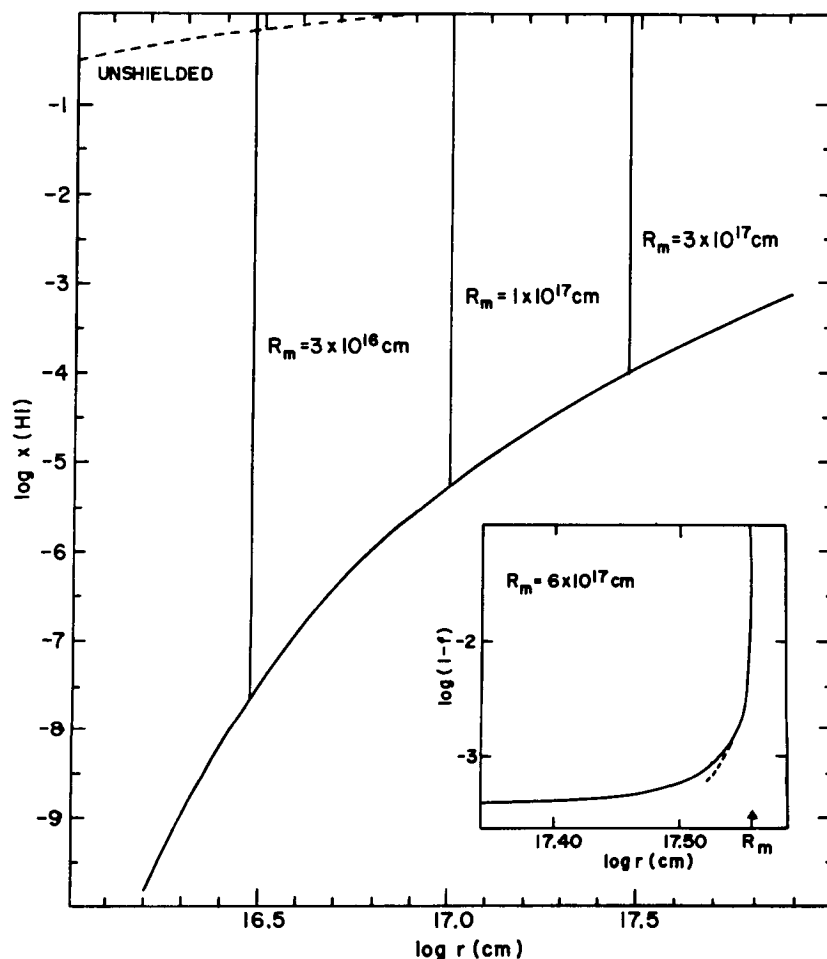


Figure 6-5. The amount of atomic hydrogen produced by the photodissociation of molecular hydrogen from the calculations of Glassgold and Huggins (1983). Three different stages of the evolution of an envelope are shown:  $t = 600, 1800$ , and  $6000$  yr or outer radii  $R_m = 0.3, 1.0$ , and  $3.0 \times 10^{17}$  cm. The parameters have been chosen to correspond to IRC + 10216. The H I abundance at each stage consists of the heavy solid curve for  $r < R_m$  plus the vertical line at  $r = R_m$ . The insert shows that the transition to  $x(\text{H I}) = 1$  at  $R_m$  is not discontinuous.

We conclude this discussion of IRC + 10216 with some brief remarks on atomic and molecular hydrogen. Molecular hydrogen has been detected by IR absorption in several very cool stars, but not in IRC + 10216. The observations are consistent with the conclusions of the discussion in the section *Thermal Equilibrium Models*, based on the variation of the  $\text{H}/\text{H}_2$  ratio in the upper atmospheres of cool stars. A more definitive conclusion requires the

calculation of the absorption-line profiles, and not just the abundances. Johnson et al. (1983) have suggested that  $\text{H}_2$  has not been observed in some stars with effective temperatures somewhat above 2500 K because they may have chromospheres.

The fact that the 21-cm line has not yet been detected in CS shells is probably consistent with currently available sensitivity. In IRC + 10216, the upper limit in the column density of  $6 \times$



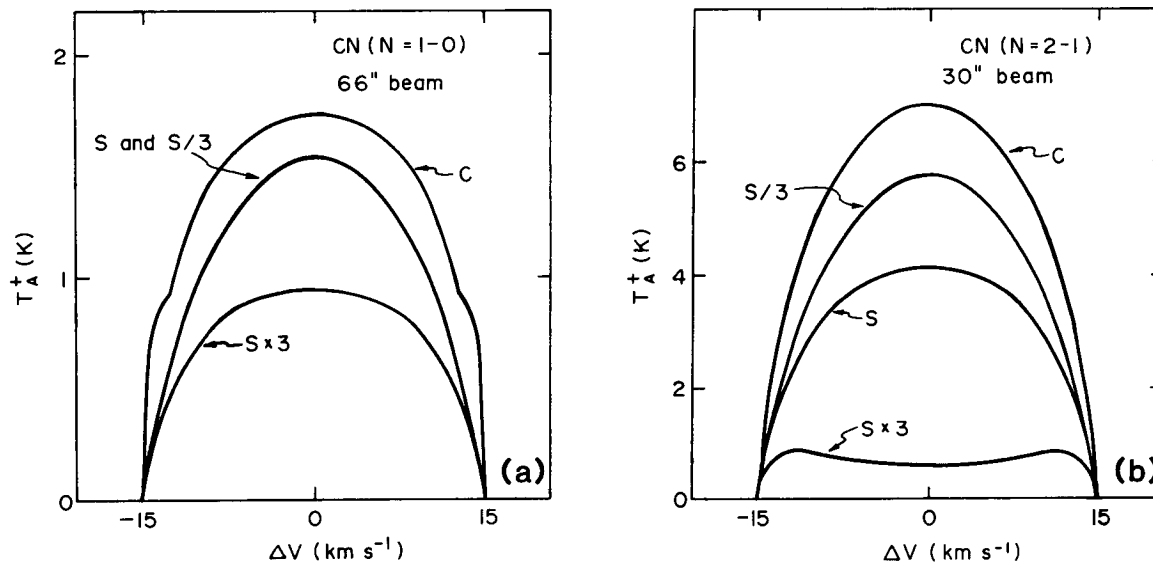


Figure 6-6. Photochemical model on-source line profiles for: (a)  $N = 1-0$  and (b)  $N = 2-1$  transitions for the CN radical (Huggins et al., 1984b) adapted to the Kitt Peak National Radio Astronomy Observatory and Owens Valley Radio Observatory beams, respectively. Curves C are for a constant abundance  $1.3 \times 10^{-6}$ , S for a "standard" set of model parameters, and S/3 and SX3 for dust shielding three times less and three times more effective than standard. The observations are fit best by a variable abundance model similar to the SX3 curves.

$10^{18} \text{ cm}^{-2}$  determined by Zuckerman et al. (1980) corresponds to an upper limit to the H I mass of  $1.1 \times 10^{31} \text{ g}$ , using a distance of 290 pc. Table 6-2 gives the H I contributions expected from the different regions of the star and its CS shell (Glassgold and Huggins, 1983). The total amount of H I produced by photodissociation is  $4 \times 10^{29} \text{ g}$ , well below the current observed upper limit. On the other hand, the small fractional abundance of atomic H injected into the envelope after freeze-out gives roughly  $1 \times 10^{31} \text{ g}$ , about the observational limit. Of course, the theoretical estimate is uncertain because of the limitations in stellar atmosphere calculations, but new higher sensitivity searches for H I in IRC + 10216 are called for.

Much less is known about molecular abundances in O-rich stars. As discussed in the section *Observations*, the CO measurements have been used to determine mass-loss rates for O-rich and C-rich stars on the assumption of solar

abundances. We have already discussed the significance of the low SiO abundances in the section *Studies of Chemical Reactions* (i.e., most of the silicon is probably incorporated into grains). As for detailed studies of the spatial distribution of molecules in O-rich shells, the main body of information consists of interferometer studies of the OH masing regions.

Unfortunately, the OH maser maps are not directly interpretable into abundance information because of the complexities of the maser emission mechanism. However, the maser models require a substantial OH abundance in the emitting regions. To account for this, Goldreich and Scoville (1976) have proposed that the OH is produced from the photodestruction of  $\text{H}_2\text{O}$ , and further studies of this model have been made by Deguchi (1982) and Huggins and Glassgold (1982b). Because the size of the  $\text{H}_2\text{O}$  distribution is determined by the amount of shielding and the photoproducted OH is distributed in a shell about the  $\text{H}_2\text{O}$ , the photo

**Table 6-2**  
**Sources of Atomic Hydrogen in IRC + 10216**

Photosphere	2.1 (29) g
Injected into envelope	~ 1 (31)
H <sub>2</sub> photodissociation in shell interior	1.5 (29)
H <sub>2</sub> photodissociation at shell surface	1.9 (29)
Photodissociation of hydrocarbons	~ 2 (28)
Total from photodissociation	4 (29)
Upper limit of Zuckerman et al. (1980)	1.1 (31)

model predicts a specific correlation between the size of the OH shell and mass-loss rate. The observed maser map sizes correlate with mass-loss rate, as was noticed first by Bowers et al. (1981), and to that extent are supportive of the models. Deguchi has argued that destruction of H<sub>2</sub>O molecules in collisions with grains, a possible alternative source of OH production, is probably unimportant.

Morris and Jura (1983b) have developed an interesting variation in the photochemical model for the unusual OH/IR supergiant, NML Cygnus. They explain the observed axially symmetric radio continuum emission (Habing et al., 1982) in terms of the ionizing radiation from the nearby Cyg OB association. Jura (1983b) has also considered dust and self-shielding of anisotropic molecular outflows.

The case of  $\alpha$  Ori holds particular interest because of the large and diverse body of data which exists on its circumstellar envelope. A coherent theoretical treatment of the observations does not exist, however, and we focus on a few issues relating to the photochemistry of its outer envelope.

As discussed in the section *Observations*, CO is the only molecule detected in this CS envelope. Its IR absorption occurs at two velocities, 10 and 16 km s<sup>-1</sup>; the weak 1.3 mm ( $J = 2-1$ ) emission is at the higher velocity and seems to be confined to within 10" (i.e.,  $3 \times 10^{16}$  cm if the distance is taken to be 200 pc). On the

other hand, scattered K I resonance radiation and polarized light are observed much farther out, 60" and 90", respectively. The dust shell, which appears to begin at about  $10 R_*$ , or  $8 \times 10^{14}$  cm, appears to be rather thin, producing a weak silicate feature and no more than a few tenths of a magnitude of visual extinction. Among the various atomic lines observed in this star, the radial profile of scattered K I radiation (see the section *Heavy Atoms*) appears to have significant potential for understanding the outer shell.

Jura and Morris (1981) made the first serious attempt to utilize the information in the CO emission-line profile and the distribution of the scattered K I line radiation. They solved time-dependent rate equations for these two species, which they linked in an interesting way. In their theory, the abundance of K I is determined by photoionization by interstellar UV radiation and by radiative recombination. The electrons are assumed to come primarily from the photoionization of C, with the fractional contribution from other heavy elements restricted to be  $1 \times 10^{-6}$ . The photochemical model enters in that the C comes from the photodissociation of CO. Jura and Morris determined the mass-loss rate of  $\alpha$  Ori to be  $1.5 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$  from the K I distribution and the assumption that the abundance of potassium is solar. From the CO emission, they determined the abundance of carbon to be  $1.25 \times 10^{-5}$ , assuming that all the carbon is in CO.

This attractive theory may serve as the first step in a more general approach to understanding the  $\alpha$  Ori shell. The effects of the chromospheric radiation will have to be included because, in many cases, photo rates calculated at the photosphere are  $\sim 10^6$  larger than those for the interstellar radiation field. The chemical reactions investigated by Clegg et al. (1983a) are also relevant, and time-dependent calculations are required in some cases. Consideration should also be given to the atomic column densities (e.g., as measured by Hagen, 1978; and Bernat, 1977), which provide important information on the ionization and gaseous abundances.

## CONCLUSIONS

The foregoing discussion shows that the study of the outer envelopes of cool evolved stars has become an active area of research. Observations at many wavelength bands are relevant—from the ultraviolet to the radio, although infrared and millimeter-wave techniques are especially useful. Future investigations with new high-resolution methods (both spatial and spectral) should be particularly significant for understanding these small, but now resolvable, structures. Although relatively little theoretical research has been done thus far, a number of interesting initiatives have been made.

Extensive observations of specific objects should be particularly useful for the development of theoretical models, as exemplified by the case of IRC + 10216. In the future, it will be important to obtain equally detailed information for other C-rich stars and for O-rich stars as well: IRC + 10216 has attracted most of the theoretical attention thus far, but perhaps it is not as typical as usually believed.

Recent theoretical considerations show that the thermal equilibrium model is of limited use for understanding the chemistry of the outer CS envelopes. Indeed, their small sizes and moderate expansion velocities indicate that time-dependent considerations dominate this subject. At the present time, we only have the results of time-dependent chemical studies for situations in which photodestruction of atoms and molecules dominate particle reactions. One clear result of the photochemical models is that molecules cannot survive very long after they reach the outer edges of isolated CS envelopes, even if they are quite thick. In other words, interstellar molecules must be produced locally within clouds because CS molecules will be destroyed within envelopes embedded in an ultraviolet radiation field. This is in contrast to dust grains, which are able to survive passage through CS envelopes. The possibility also exists that sufficiently detailed measurements of gas-phase species in circumstellar envelopes could provide some insights into the formation of the CS dust. Finally, the theoretical model-

ing of the chemistry of CS envelopes provides quantitative tests of chemical concepts which have a broader interest than the envelopes themselves. In certain cases, the observations confirm the density and velocity profiles characteristic of a constant and spherically symmetric mass loss, so that the physical and chemical problems can be investigated with known flow conditions. Such situations rarely occur in the study of interstellar chemistry, so that, in a sense, CS envelopes provide a better controlled chemical laboratory than interstellar clouds.

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## NOTE ADDED IN PROOF

Since the review was completed in 1984, there have been a number of new observations and theoretical investigations of circumstellar chemistry. We mention briefly here some of the main results.

In IRC + 10216, a second ring molecule  $C_3H_2$  has been added to the list of detected species (Matthews and Irvine, 1985; Thaddeus et al., 1986); a new free radical has also been found (Guelin et al., 1986), but the exact carrier of the lines has not been identified. Observations of CRL 2688 with the new 30-m IRAM telescope (Lucas et al., 1986) have shown that lines previously seen only in IRC + 10216 can now be detected in other CSEs so that the detailed intercomparison of the chemistry of different objects is now a real possibility. One main theoretical development of carbon-rich envelopes has been the exploration of the role of atomic and molecular ions by Nejad et al. (1984) and Glassgold et al. (1986). The latter have developed a model for the distribution of

molecular ions in IRC + 10216 which is consistent with new limits on the abundance of  $\text{HCO}^+$  reported by Lucas et al. (1986). Jura and Morris (1985) have investigated the condensation of molecules onto the dust in the outflowing winds.

In oxygen-rich stars, both  $\text{SO}_2$  (Lucas et al., 1986) and HCN have been detected (Deguchi and Goldsmith, 1986), so for these objects, the number of observed species is beginning to approach a level where quantitative comparison with theory becomes interesting. In the CSE of  $\alpha$  Ori, CO in the CSE (Huggins, 1985) and C/H in the photosphere (Lambert et al., 1984) have been reevaluated: C appears to normal in the photosphere, and CO is probably underassociated in the envelope. The role of chromospheric radiation has been discussed by Glassgold and Huggins (1986), and their model gives a satisfactory account of the available KI scattering data.

It seems clear from these latest developments that rapid progress can be expected in many areas of circumstellar chemistry in the next few years.

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